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Titration microcalorimetry of mixed alkyltrimethylammonium bromide surfactant aqueous solutions

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Enthalpograms recorded using a titration microcalorimeter are reported for mixtures of surfactants hexadecyltrimethylammonium bromide (CTAB) and tetradecyltrimethylammonium bromide (TTAB) in aqueous solutions at 298.2 K. The enthalpograms for each mixture show that the micellar phase comprises a mixture of the surfactants rather than separate domains comprising single surfactants. The enthalpograms are satisfactorily accounted for using the pseudo-phase model taking account of the non-ideal properties of the mixed micellar phase and of the mixed aqueous surfactant solutions. A quantitative treatment is described for the analysis of titration calorimetric results for mixed ionic surfactant systems. For the micellar phase a key parameter determining the critical micellar concentration (c.m.c.) is a generalised rational activity coefficient for the micellar phase. For the systems described here this parameter is less than unity indicating that surfactant–surfactant interactions stabilise the micellar phase, whereas a generalised Gibbs energy surfactant–surfactant interaction parameter for the aqueous phase is positive, opposing Debye–Hückel ionic-atmosphere stabilising effects although the corresponding enthalpic parameter is exothermic. As the total concentration of surfactant in the sample cell of the calorimeter increases during a given experiment, the calculated c.m.c. changes as a consequence of these interactions which are a function of composition. In general terms the c.m.c. and enthalpy of mixed micelle formation for the CTAB–TTAB mixture change smoothly between the corresponding properties of the two pure surfactants.

Introduction

Titration microcalorimetry¹ of aqueous solutions containing surfactants including alkyltrimethylammonium bromides,² 4-alkyl-1-pyridinium halides³ and sugar-based surfactants⁴ has proved a valuable technique for characterising surfactants in terms of their c.m.c.s and enthalpies of micelle formation. In these experiments the aqueous surfactant solutions contained a single surfactant. A recent product report⁵ noted that the ingredient market for household detergents will grow to \$8.2 billion by the year 2001. Interestingly the required list of contents shows that many household products contain a mixture of surfactants. At first sight therefore titration microcalorimetry should provide a source of important information concerning mixed surfactant solutions. Unfortunately thermodynamic analysis of the properties of such systems is complicated, thereby tending to counter this optimistic prediction. Here we describe a thermodynamic treatment which forms a satisfactory basis for the analysis of titration microcalorimetric results for mixed surfactant systems.

Thermodynamic treatments of mixed micellar systems fall into two groups which we designate Type A and Type B. These types are readily distinguished by considering solutions prepared using two surfactants X and Y. These two surfactants in separate aqueous solutions (at defined T and p) having thermodynamic properties which are, for the moment, assumed to be ideal can be characterised by c.m.c.s $c_{\text{m.c.}}^{\text{X}}$ and $c_{\text{m.c.}}^{\text{Y}}$ and standard enthalpies of micelle formation, $\Delta_{\text{mic}}H_{\text{X}}^{\circ}$ and $\Delta_{\text{mic}}H_{\text{Y}}^{\circ}$. In a given mixed very dilute aqueous solution, surfactants X(aq) and Y(aq) are monomeric. More surfactant, both X and Y, is added until at some point a microscopic

amount of micellar phase appears. The solution is characterised by a c.m.c. for the mixed surfactant, $X + Y$. In the aqueous solution the concentrations of X and Y are $c_{\text{m.c.}}^{\text{X}}$ and $c_{\text{m.c.}}^{\text{Y}}$ respectively, the extent to which the latter differ from $c_{\text{m.c.}}^{\text{X}}$ and $c_{\text{m.c.}}^{\text{Y}}$ being important but unknown *a priori*. But since only microscopic amounts of surfactants are present as the micellar phase, the c.m.c.s of X and Y are simply related to the volume of the aqueous solution and the amounts of surfactants X and Y used in the preparation of the solution. We identify treatments based on this description of mixed surfactant systems as Type A. For example, Type A equations are described by Clint⁶ and by Lange and Beck,⁷ yielding estimates of the c.m.c. for a mixed surfactant as a function of $c_{\text{m.c.}}^{\text{X}}$, $c_{\text{m.c.}}^{\text{Y}}$ and the mole fraction α_{X} of surfactant X in the mixed surfactant. Warr and coworkers⁸ used this approach in an investigation of c.m.c.s for nonylphenol ethoxylates. The treatment described by Clint⁶ assumes that the thermo-dynamic properties of the mixed micellar phase are ideal. The analysis can be extended to take account of surfactant–surfactant interactions in the micellar phase using simple regular solution theory.^{9–11}

To the solution described above, more surfactants X and Y are added such that the amounts of X and Y in the micellar phase increase. As more surfactant mixture is added to the solution, surfactants X and Y distribute between aqueous and micellar phases. Moreover the distribution is expected to depend on the nature of the surfactants and on the total amounts of X and Y in the two-phase system. To a first approximation the amounts of surfactants X and Y present as monomers stay constant, the added surfactants merely increasing the amounts present in the micellar phase.¹⁰ We identify treatments based on this approach as Type B.

In summary, a Type A description does not form a satisfactory basis for analysis of titration calorimetric results because the calorimetric experiments start with solutions in the injected aliquots (see below) where the concentration of surfactants significantly exceeds the c.m.c. of the solutions under investigation. In other words analysis of titration microcalorimetric results for mixed surfactant systems requires a Type B approach. The first stage of the analysis described here concentrates on equations for the c.m.c. of mixed micellar systems. In the second stage we use the calculated compositions to describe the change in enthalpy when more surfactants are added in the form of a quite concentrated solution containing both surfactants X and Y.

For the Type B approach, the derived equations are complicated.^{12,13} The equations are simplified if it can be assumed that the thermodynamic properties of the system are ideal. However for mixed surfactant systems the enthalpograms show that this assumption is unrealistic. Here we describe an analysis using as a starting point the equations derived by Clint⁶ but modified to take account of the non-ideal thermodynamic properties of micellar and aqueous phases. Even so, four activity coefficients are required to take account of surfactant-surfactant interactions in both aqueous and micellar phases. In addition, the analysis requires several enthalpic interaction parameters in order to calculate the heats accompanying injection of aliquots into the sample cell. The calculation must also take account of the change in composition of the sample cell throughout the sequence of injections.

The starting point of the calculations reported here is the previously determined c.m.c.s and enthalpies of micelle formation for the two surfactants and the composition of the injected aliquot containing the mixed surfactant system. In order to make progress we found it necessary to make some simplifying assumptions. For a given surfactant system, we use a rational activity coefficient of the surfactants in the micellar phase as an adjustable parameter. The enthalpies of the two components of the micellar phase are described using an adjustable enthalpic parameter together with an equation based on regular solution theory.^{9,13-17} The properties of the mixed aqueous surfactant solutions are described using the Debye-Hückel Limiting Law in which an equation for $\ln(\gamma_j)$ is extended with an adjustable parameter linear in total surfactant concentration; γ_j is the mean ionic activity coefficient for the mixed (surfactant) salt in aqueous solution. The enthalpies of micelle formation at each stage of the experiment are calculated using the mol% weighted enthalpies of the pure surfactants plus an adjustable enthalpic interaction parameter term describing surfactant-surfactant interactions in aqueous solution. We show that using this reduced set of parameters, the calculated enthalpograms show satisfactory agreement with those recorded. We conclude that the approach described

here forms a basis for probing the thermodynamic properties of mixed aqueous surfactant systems.

Titration microcalorimetry

In a typical microcalorimetric experiment,²⁻⁴ small aliquots (*e.g.* volume 5×10^{-6} dm³) of a solution containing surfactants are injected, under computer control, into a sample cell (*e.g.* volume 1.5 cm³). Then at each injection the amount of surfactant *j* in the sample cell increases by an amount n_j mol. The microcalorimeter records the ratio of heat *q* to the amount n_j , hence yielding the enthalpy of injection at injection numbers from *I* = 1 to, for example, *I* = 50. The outcome of the experiment is summarised in a plot of $\Delta_{\text{inj}} H(I+1)$ against either injection number (*I* + 1) or total concentration of surfactant *j* in the sample cell, $c_j(I+1)$, *e.g.* Fig. 1. In a typical case involving a single surfactant CTAB, the enthalpogram has a straightforward pattern; see Fig. 4 of ref. 2. The pattern can be understood along the following lines where we assume for the moment that the thermodynamic properties of the aqueous solution and micellar phase are ideal. We adopt the pseudo-separate phase mode^{3,18,19} for surfactant solutions such that there exists at equilibrium (i) monomer surfactants in aqueous solution and (ii) pure surfactant in a micellar phase. If c.m.c._{*j*}⁰ for the surfactant is very low, the contribution of surfactant to the enthalpy of the concentrated aliquot system equals $n_j H_j^* H_j^*(\text{mic})$ where $H_j^*(\text{mic})$ is the molar enthalpy of surfactant *j* in the micellar phase. At low injection numbers, all surfactant in the sample cell is in the form of monomeric solutes in aqueous solution. Then the contribution of the surfactant to the enthalpy of the solution of the sample cell at injection number *I*, $H(I) = \{I n_j \phi(H_j)^\infty\}$ where $\phi(H_j)^\infty$ is the limiting apparent molar enthalpy of solute *j* in aqueous solution. Similarly at injection number (*I* + 1), $H(I+1) = \{(I+1)n_j \phi(H_j)^\infty\}$. Then heat $q [=H(I+1) - H(I) - H(\text{inj})]$ is given by $\{n_j [-H_j^*(\text{mic}) + \phi(H_j)^\infty]\}$. Hence $\{q/n_j\}$ at (*I* + 1) = $[-H_j^*(\text{mic}) + \phi(H_j)^\infty]$ which equals $-\Delta_{\text{mic}} H_j^0$, where $\Delta_{\text{mic}} H_j^0$ is the standard enthalpy of micelle formation, being the change in enthalpy when one mole of surfactant transfers from the monomeric standard state in aqueous solution to the standard state in the micellar phase. Thus at low injection numbers the dominant process is micelle deaggregation.²⁰ At high injection numbers, all surfactants in the sample cell are, using the assumptions described above, in the micellar phase such that the ratio $\{q/n_j\}$ at (*I* + 1) is approximately zero. In summary the switch in the shape of the enthalpogram from $\Delta_{\text{mic}} H_j^0$ to effectively zero at a certain injection number leads to estimates of both the c.m.c. and $\Delta_{\text{mic}} H_j^0$. In the experiments envisaged here the solution in the syringe contains both surfactants X and Y at a concentration above the c.m.c. of the

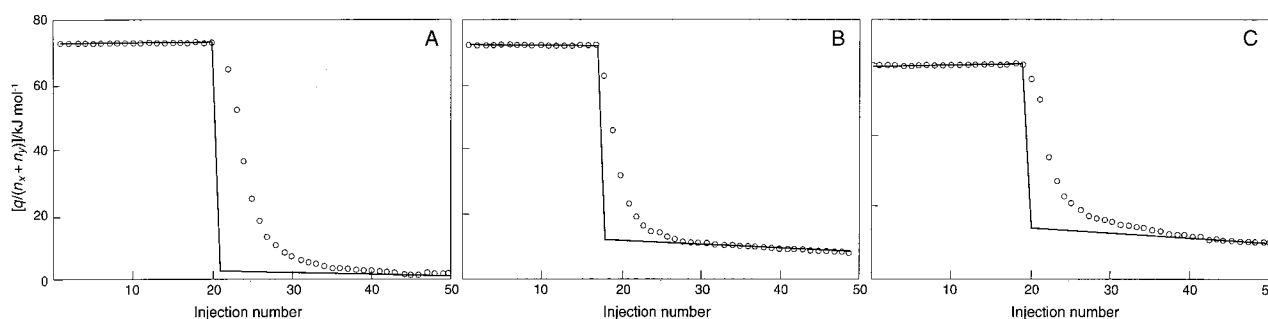


Fig. 1 Comparison of recorded and calculated enthalpograms for aqueous solutions at 298.2 K containing mixtures of surfactants CTAB and TTAB; 50 injections of aliquots volume 5×10^{-6} dm³ into the sample cell, volume 1.411 cm³ containing initially water; A, 70 mol% CTAB; amount of CTAB = 4.9×10^{-8} mol and amount of TTAB in each aliquot = 2.0×10^{-8} mol; B, 50 mol% CTAB; concentration of mixed surfactant in each injected aliquot = 20×10^{-3} mol dm⁻³; total amount of surfactants in each aliquot = 10×10^{-8} mol; the amounts of CTAB and TTAB in each aliquot = 5.0×10^{-8} mol; C, 30 mol% CTAB; as in (B) except total amount of surfactant in each aliquot = 11.5×10^{-8} mol; amount of CTAB = 3.45×10^{-8} mol and amount of TTAB in each aliquot = 8.05×10^{-8} mol.

mixed solution. The ratio of amounts $n(X)$ to $n(Y)$ in the syringe is a new variable.

Experimental

Materials

The alkyltrimethylammonium bromides were those used in previous studies.^{2,3}

Calorimeter

A titration microcalorimeter (MicroCal. Ltd., USA) was used as previously described.^{2,3} The volume of the sample cell was 1.411 cm³; the volume of the injected aliquot for the series of experiments reported here was 5×10^{-6} dm³. The temperature of the sample cell and injected aliquot was set at 298 K. The sequence of injections was under computer control (PC). The time step between injections was set such that the solution in the sample cell recovered thermodynamic equilibrium before another aliquot was injected. This condition was recorded as a small amount of 'baseline' between injections. The pulse traces recorded by the microcalorimeter showed the rate of heating as a function of time. These traces were integrated to produce a plot of heat q as a function of injection number (or, concentration of surfactants in the sample cell). We commented above on the shape of the enthalpograms in the case of CTAB(aq). In these experiments the concentration of CTAB(aq) in the aliquot is such that at roughly the 25th injection for a protocol set up for 50 injections the concentration of CTAB in the sample cell is near the c.m.c. However with reference to an investigation of mixed surfactant systems there is an important consideration. In a perfect series of experiments the total concentration of mixed surfactant in the injected aliquot would be kept constant. The obvious protocol would be to vary the molar ratio of the two surfactants across the range from zero to unity for one surfactant. For each enthalpogram the optimum set of experiments might show a change in pattern on going from, say, low to high injection numbers with change in composition of the aliquots. Unfortunately the change in c.m.c. with molar ratio often means that this approach to the planned experiments fails. If the concentration of surfactant in the injected aliquot is just above the c.m.c., the calorimeter records the heat of deaggregation but there is no break in pattern because the concentration of surfactant in the sample cell never exceeds the c.m.c. Hence the c.m.c. is not determined. On the other hand if the concentration of surfactant in the injected aliquot exceeds significantly the c.m.c., the concentration of surfactant in the sample cell exceeds the c.m.c. after the first one or two injections. Therefore estimates of both the c.m.c. and enthalpy of micelle formation are imprecise. These considerations are important in a study of mixed surfactant systems because there is no alternative to experimental protocols which require different concentrations of surfactants in the injected aliquots when the properties of mixed surfactants are being studied. Further, there is an obvious need for preliminary experiments in order to arrive at the optimum conditions. These comments account for the fact that in the series of typical experiments summarised in Fig. 1, the concentrations of mixed surfactants in the injected aliquots differ.

Results

Enthalpograms for solutions containing a single surfactant were previously reported; *e.g.* Fig. (4) in ref. 2 for CTAB(aq). Typical enthalpograms for three mixtures of CTAB and TTAB are shown in Fig. 1. In the case of the mixtures, the injection number corresponding to the sharp fall in the ratio $[q/(n_X^0 + n_Y^0)]$ is identified as the injection number at which a

micellar phase first appears in the sample cell. The ratio $[q/(n_X^0 + n_Y^0)]$ at high injection numbers is significantly smaller than the ratio at low injection numbers. Consequently the latter yields an estimate of the enthalpy of micelle formation, $\Delta_{\text{mic}}H$ for a given mixture. van Os plots²¹ of $\sum_{j=1}^{j=I} [q/(n_X^0 + n_Y^0)]$ against injection number I yield an estimate of the c.m.c. for a given mixture; *e.g.* Fig. 2. Over the first set of injection numbers a plot of $\sum_{j=1}^{j=I} [q/(n_X^0 + n_Y^0)]$ against injection number I forms a straight line. Over the set of high injection numbers a plot of $\sum_{j=1}^{j=I} [q/(n_X^0 + n_Y^0)]$ against injection number I forms a straight line although, because the magnitude of each recorded heat is smaller, the slope of this line is smaller than that for the plot over low injection numbers. The two plots intersect at the c.m.c. as defined by the van Os method²¹ where the change in $\sum_{j=1}^{j=I} [q/(n_X^0 + n_Y^0)]$ is smooth over a small number of injection numbers. The plot illustrates the way in which the plots in Fig. 1A–C perhaps over-emphasise the transition between recorded heat between high and low injection numbers. Estimates of $\Delta_{\text{mic}}H$ and c.m.c. are summarised in Table 1 for several mixed CTAB–TTAB aqueous systems at 298.2 K. The c.m.c.s were determined using van Os plots obtained from at least three titrations for a given system. The estimates of $\Delta_{\text{mic}}H$ are the ratios $\sum_{j=1}^{j=I} [q/(n_X^0 + n_Y^0)]$ recorded at low injection numbers, Fig. 1. We have taken these values as good estimates of the limiting enthalpy of micelle formation, $\Delta_{\text{mic}}H^\infty$. The titration plots offer a sound estimate of the latter if $\sum_{j=1}^{j=I} [q/(n_X^0 + n_Y^0)]$ at high injection numbers is close to zero. However this is not the case for the CTAB–TTAB mixtures because the thermodynamic properties of solutions in the sample cell and injected aliquots are not ideal; see below. We also comment below on the estimates of c.m.c. because new features emerge from the calculations.

Analysis: Critical micellar concentrations

In terms of the pseudo-separate phase model,^{18,19} the phase equilibrium in an aqueous solution containing a single surfactant X is characterised by the balance of equilibrium chemical potentials (at fixed temperature and pressure) describing surfactant X in aqueous solution at a concentration c.m.c._X, $\mu_X(\text{c.m.c.}_X; \text{aq})$ and in the pure micellar phase $\mu_X^*(\text{mic})$; eqn. (1)

$$\mu_X(\text{c.m.c.}_X; \text{aq}) = \mu_X^*(\text{mic}) \quad (1)$$

A similar equation describes an aqueous solution containing only surfactant Y.

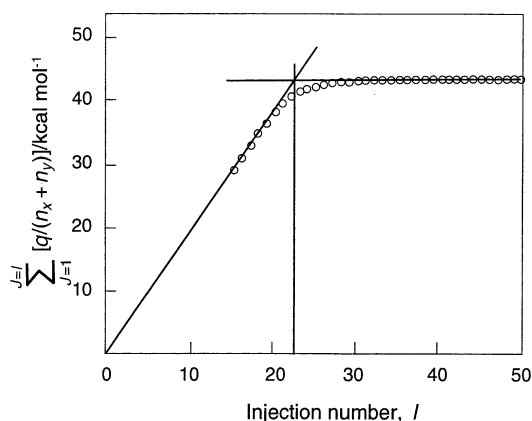


Fig. 2 Typical van Os plot for aqueous mixtures of CTAB and TTAB surfactants showing the dependence of $\sum_{j=1}^{j=I} [q/(n_X^0 + n_Y^0)]$ on injection number for the enthalpogram of the surfactant mixture containing 80 mol% CTAB; concentration of mixed surfactant in each injected aliquot = 14×10^{-3} mol dm⁻³; total amount of surfactants in each aliquot = 7×10^{-8} mol; amount of CTAB = 5×10^{-8} mol and amount of TTAB = 1.4×10^{-8} mol.

Table 1 Derived parameters for mixtures of CTAB and TTAB surfactants^a in aqueous solutions at 298.2 K

CTAB (mol%)	c.m.c. ^b /mol m ⁻³	$-H_{\text{mic}}H^0/\text{kJ mol}^{-1}$	$U/\text{kJ mol}^{-1}$	$-h_{\text{xy}}/\text{kJ mol}^{-1}$
80	1.13 ± 0.01	7.92 ± 0.07	-0.1	5.0
70	1.19 ± 0.01	7.35 ± 0.06	0.5	5.0
60	1.32 ± 0.01	6.58 ± 0.09	2.5	6.0
50	1.42 ± 0.01	7.24 ± 0.08	-0.6	12.0
40	1.60 ± 0.01	6.64 ± 0.07	0.5	14.0
30	1.85 ± 0.03	6.18 ± 0.25	2.0	12.0
20	2.43 ± 0.01	6.11 ± 0.10	-1.8	14.0
10	3.21 ± 0.02	5.76 ± 0.10	-1.8	14.0

^a For CTAB: c.m.c. = 1.02 ± 0.02 mol m⁻³; $\Delta_{\text{mic}}H^0 = -8.50 \pm 0.29$ kJ mol⁻¹; for TTAB: c.m.c. = 4.11 ± 0.08 mol m⁻³; $\Delta_{\text{mic}}H^0 = -4.49 \pm 0.09$ kJ mol⁻¹. ^b Obtained from van Os plots; average of three determinations. ^c Calculated as $[q/(n_{\text{x}}^0 + n_{\text{y}}^0)]$ at low injection numbers with no correction for $[q/(n_{\text{x}}^0 + n_{\text{y}}^0)]$ at high injection numbers; average of three recorded enthalpograms.

A given real aqueous system containing surfactant X is prepared using n_{x}^0 moles of surfactant X in volume V; concentration $c_{\text{x}}^0 = n_{\text{x}}^0/V$ where the amount of surfactant X in the aqueous phase equals V c.m.c._X. Hence the amount of surfactant X present in the micellar phase, $n_{\text{x}}(\text{mic}) = n_{\text{x}}^0 - V$ c.m.c._X. Then

$$n_{\text{x}}(\text{mic})/V = c_{\text{x}}^0 - \text{c.m.c.}_X \quad (2)$$

For a mixed surfactant system, eqn. (2) is based on a Type B description because we envisage an experiment in which small aliquots of the surfactants are added continually to the system to well beyond the stage at which the micellar phase first appears in the sample cell. The term $n_{\text{x}}(\text{mic})/V$ is the ratio of the amount of surfactant X in the micellar phase to the volume of the system. In the micellar phase the amounts of the two surfactants are $n_{\text{x}}(\text{mic})$ and $n_{\text{y}}(\text{mic})$. The composition of the binary micellar phase is characterised using mole fractions, $x_{\text{x}}(\text{mic})$ and $x_{\text{y}}(\text{mic})$ [$= 1 - x_{\text{x}}(\text{mic})$]. Thus

$$x_{\text{x}}(\text{mic}) = n_{\text{x}}(\text{mic})/[n_{\text{x}}(\text{mic}) + n_{\text{y}}(\text{mic})] \quad (3)$$

Taking account of both aqueous and micellar phases, the (global) mole fractions, are $\alpha_{\text{x}} = n_{\text{x}}^0/[n_{\text{x}}^0 + n_{\text{y}}^0]$ and $\alpha_{\text{y}}[1 - \alpha_{\text{x}}]$. The distinction between for example, α_{x} and $x_{\text{x}}(\text{mic})$ is important. 'Mole fractions' α_{x} and α_{y} do not involve the solvent, water in the aqueous phase. The amount of surfactant X in the aqueous phase at c.m.c._X, $n_{\text{x}}(\text{aq}; \text{c.m.c.}_X)$ equals $V/\text{c.m.c.}(\text{mix}) - n_{\text{x}}(\text{aq}; \text{c.m.c.}_X)$. The amount of surfactant X in the micellar phase, $n_{\text{x}}(\text{mic}) = n_{\text{x}}^0 - n_{\text{x}}(\text{aq}; \text{c.m.c.}_X)$. Then with $n_{\text{y}}(\text{mic}) = n_{\text{y}}^0 - n_{\text{y}}(\text{aq})$,

$$x_{\text{x}}(\text{mic}) = [n_{\text{x}}^0 - n_{\text{x}}(\text{aq}; \text{c.m.c.}_X)]/[n_{\text{x}}^0 + n_{\text{y}}^0 - V\text{c.m.c.}(\text{mix})] \quad (4)$$

By definition, $c_{\text{x}}^0(\text{tot}) = n_{\text{x}}^0(\text{tot})/V$ and $c_{\text{y}}^0(\text{tot}) = n_{\text{y}}^0(\text{tot})/V$. Then,

$$c^0(\text{tot}) = c_{\text{x}}^0(\text{tot}) + c_{\text{y}}^0(\text{tot}) \quad (5)$$

From eqn. (4),

$$x_{\text{x}}(\text{mic}) = [c_{\text{x}}^0 - \text{c.m.c.}_X]/\{c^0(\text{tot}) - [\text{c.m.c.}_X + \text{c.m.c.}_Y]\} \quad (6)$$

The mole fraction composition of the mixed micellar phase is related to the overall concentrations of the surfactants, $c^0(\text{tot})$, $c_{\text{x}}^0(\text{tot})$, $c_{\text{y}}^0(\text{tot})$ and the parameters characterising the aqueous solutions, c.m.c._X and c.m.c._Y. With $c_{\text{x}}^0 = \alpha_{\text{x}}c^0(\text{tot})$, then as shown by Clint⁶ {see also ref. 13, eqn. (8)}.

$$x_{\text{x}}(\text{mic}) = [\alpha_{\text{x}}c^0(\text{tot}) - \text{c.m.c.}_X]/\{c^0(\text{tot}) - [\text{c.m.c.}_X + \text{c.m.c.}_Y]\} \quad (7)$$

Eqn. (7) relates the mole fraction composition of the micellar phase to two quantities which are known 'a priori', α_{x} and $c^0(\text{tot})$. However c.m.c._X and c.m.c._Y are unknown.

In order to make progress we exploit thermodynamic descriptions of the system. We envisage a given system (at defined T and p) prepared using surfactants X and Y in volume V . A micellar phase spontaneously forms containing surfactants X and Y. At equilibrium, two conditions are met; (i) $\mu_{\text{x}}(\text{c.m.c.}_X; \text{aq}) = \mu_{\text{x}}(\text{mic})$, and (ii) $\mu_{\text{y}}(\text{c.m.c.}_Y; \text{aq}) = \mu_{\text{y}}(\text{mic})$.

In the mixed micellar solution, the concentration of surfactant X in aqueous solution is c.m.c._X(aq) and hence the chemical potential $\mu_{\text{x}}(\text{aq})$ is given by eqn. (8) where $c_{\text{r}} = 1$ mol dm⁻³.

$$\mu_{\text{x}}(\text{mic}) = \mu_{\text{x}}^0(\text{aq}) + RT \ln[\text{c.m.c.}_X(\text{aq})y_{\text{x}}(\text{aq})/c_{\text{r}}] \quad (8)$$

Thus $\mu_{\text{x}}^0(\text{aq})$ is the chemical potential of X(aq) in an aqueous solution having unit concentration and ideal thermodynamic properties (at the same T and p). Activity coefficient $y_{\text{x}}(\text{aq})$ accounts for the fact that the thermodynamics properties of surfactant X in the aqueous solutions are not ideal. A similar equation describes the properties of surfactant Y.

In the event that the micellar pseudo-phases formed by surfactants X and Y are completely immiscible then $\mu_{\text{x}}(\text{mic})$ in eqn. (1) would be replaced by $\mu_{\text{x}}^*(\text{mic})$; cf. eqn. (1). In fact we envisage that the micellar pseudo-phases formed by surfactants X and Y are completely miscible, such that the micellar phase resembles a binary liquid mixture in which the chemical potentials $\mu_{\text{x}}(\text{mic})$ and $\mu_{\text{y}}(\text{mic})$ are related to the mole fraction composition and rational activity coefficients for both components at fixed T and p . If the thermodynamic properties of the micellar phase are ideal (i.e. $f_{\text{x}}(\text{mic}) = f_{\text{y}}(\text{mic}) = 1$, at all mole fraction compositions) then $\mu_{\text{x}}(\text{mic})$ would decrease gradually with decrease in $x_{\text{x}}(\text{mic})$ and $\mu_{\text{y}}(\text{mic})$ would decrease with decrease in $x_{\text{y}}(\text{mic})$, the molar Gibbs energy of mixing being negative.

The chemical potential of surfactant X in the micellar phase is related to the mole fraction $x_{\text{x}}(\text{mic})$ and the rational activity coefficient $f_{\text{x}}(\text{mic})$ together with the chemical potential of pure micellar X, $\mu_{\text{x}}^*(\text{mic})$ at the same T and p . Thus

$$\mu_{\text{x}}(\text{mic}) = \mu_{\text{x}}^*(\text{mic}) + RT \ln[x_{\text{x}}(\text{mic})f_{\text{x}}(\text{mic})] \quad (9)$$

Here limit [$x_{\text{x}}(\text{mic}) \rightarrow 1.0$] $f_{\text{x}}(\text{mic}) = 1.0$.

In the mixed micelle $x_{\text{x}}(\text{mic}) < 1.0$, there is "communication" between surfactants X and Y in the micellar phase. At equilibrium the chemical potentials $\mu_{\text{x}}(\text{aq})$ and $\mu_{\text{x}}(\text{mic})$ are equal.

$$\begin{aligned} \mu_{\text{x}}^0(\text{aq}) + RT \ln[\text{c.m.c.}_X(\text{aq})y_{\text{x}}(\text{aq})/c_{\text{r}}] \\ = \mu_{\text{x}}^*(\text{mic}) + RT \ln[x_{\text{x}}(\text{mic})f_{\text{x}}(\text{mic})] \end{aligned} \quad (10)$$

A similar equation describes the properties of surfactant Y. For surfactant X, the change in standard Gibbs energy when one mole of surfactant X transfers from the aqueous into the micellar phase $\Delta_{\text{mic}}G_{\text{x}}^0$ is given by eqn. (11).

$$\Delta_{\text{mic}}G_{\text{x}}^0 = RT \ln\{[\text{c.m.c.}_X y_{\text{x}}(\text{aq})/c_{\text{r}}]/[x_{\text{x}}(\text{mic})f_{\text{x}}(\text{mic})]\} \quad (11)$$

Thus $f_{\text{x}}(\text{mic})$ takes account of surfactant-surfactant interactions in the mixed micellar phase. For a system containing no surfactant Y, $\Delta_{\text{mic}}G_{\text{x}}^0$ is given by eqn. (12) assuming that in the absence of Y, the thermodynamic properties of surfactant X in aqueous solution are ideal.

$$\Delta_{\text{mic}}G_{\text{x}}^0 = RT \ln\{\text{c.m.c.}_X^0/c_{\text{r}}\} \quad (12)$$

Combination of eqn. (11) and (12) yields the required equation for c.m.c._X.

$$\text{c.m.c.}_x = \text{c.m.c.}_x^0 x_x(\text{mic}) f_x(\text{mic}) / y_x(\text{aq}) \quad (13)$$

Similarly for surfactant Y,

$$\text{c.m.c.}_y = \text{c.m.c.}_y^0 x_y(\text{mic}) f_y(\text{mic}) / y_y(\text{aq}) \quad (14)$$

In other words, c.m.c._x and c.m.c._y are related to the corresponding ideal properties, the composition of the micellar phase and the extent to which the thermodynamic properties of aqueous and micellar phases differ from ideal.

Eqn. (13) and (14) are combined, noting that $x_y(\text{mic}) = [1 - x_x(\text{mic})]$.

$$\begin{aligned} \text{c.m.c.}_y &= [\text{c.m.c.}_y^0 f_y(\text{mic}) / y_y(\text{aq})] \\ &\times \{1 - [\text{c.m.c.}_x y_x(\text{aq}) / \text{c.m.c.}_x^0 f_x(\text{mic})]\} \end{aligned} \quad (15)$$

Eqn. (15) relates the two critical micellar concentrations c.m.c._x and c.m.c._y in a real surfactant system. Combination of eqn. (7) and (15) yields an equation for c.m.c._x . Then,

$$\begin{aligned} \text{c.m.c.}_x &= [\text{c.m.c.}_x^0 f_x(\text{mic}) / y_x(\text{aq})] \\ &\times [\alpha_x c^0(\text{tot}) - \text{c.m.c.}_x] / \{c^0(\text{tot}) - [\text{c.m.c.}_x + \text{c.m.c.}_y]\} \end{aligned} \quad (16)$$

In the next stage we use eqn. (15) for c.m.c._y , substituting in eqn. (16). Then,

$$\begin{aligned} \text{c.m.c.}_x &= [\text{c.m.c.}_x^0 f_x(\text{mic}) / y_x(\text{aq})] [\alpha_x c^0(\text{tot}) - \text{c.m.c.}_x] \\ &\times \left[c^0(\text{tot}) - \text{c.m.c.}_x - \frac{\text{c.m.c.}_y^0 f_y(\text{mic})}{y_y(\text{aq})} \right. \\ &\times \left. \left[1 - \frac{\text{c.m.c.}_x y_x(\text{aq})}{\text{c.m.c.}_x^0 f_x(\text{mic})} \right] \right]^{-1} \end{aligned} \quad (17)$$

Eqn. (17) is thermodynamically correct. No assumptions have been made in its derivation other than assuming the validity of the pseudo-separate phase model. Eqn. (17) can be written as a quadratic equation in the unknown c.m.c._x . Even granted that c.m.c._x^0 and c.m.c._y^0 together with $c^0(\text{tot})$ and α_x are known there are four key unknowns, $y_x(\text{aq})$, $y_y(\text{aq})$, $f_x(\text{mic})$ and $f_y(\text{mic})$, describing the extent to which the thermodynamic properties of aqueous and micellar phases are not ideal. As noted above, in order to make progress some assumptions are invoked at this stage. The aim of the analysis is to produce a calculated enthalpogram for a given surfactant system which resembles that observed. We assumed that $f_x(\text{mic})$ equals $f_y(\text{mic})$ and that both are in turn equal to $f(\text{mic})$, where $f(\text{mic})$ is characteristic of the percentage composition of the surfactant mixture but independent of the composition of the micellar phase either in the sample cell or injected aliquot. Thus $f(\text{mic})$ is an adjustable parameter. Activity coefficients $y_x(\text{aq})$, $y_y(\text{aq})$ refer to the properties of surfactants CTAB and DTAB, both 1:1 salts, in the aqueous solution. We assume that these coefficients are equal, being related to the total concentration of surfactants in the aqueous solution, $c(\text{aq; tot})$ using eqn. (18). Thus,

$$\begin{aligned} \ln\{y(\text{aq})\} &= -S_y [c(\text{aq; tot}) / c_r]^{1/2} \\ &+ [2.0 g_{xy} (c(\text{aq; tot}) / RT c_r)] \end{aligned} \quad (18)$$

Here S_y is the Debye-Hückel coefficient for aqueous solutions at 298.2 K where $c_r = 1 \text{ mol dm}^{-3}$. The coefficient g_{xy} is an adjustable parameter taking account of ion-ion interactions in the aqueous phase other than charge-charge interactions described by the Debye-Hückel Limiting Law.²² Hence the quadratic eqn. (17) takes the following form.

$$\begin{aligned} &(\text{c.m.c.}_x)^2 y(\text{aq}) [\text{c.m.c.}_y^0 - \text{c.m.c.}_x^0] \\ &+ \text{c.m.c.}_x [\{y(\text{aq}) c^0(\text{tot}) \text{c.m.c.}_x^0\} \\ &- \{y(\text{aq}) \text{c.m.c.}_y^0 f(\text{mic}) \text{c.m.c.}_x^0\} \\ &+ \{(\text{c.m.c.}_x^0)^2 f(\text{mic})\}] \\ &- [\text{c.m.c.}_x^2 f(\text{mic}) \alpha_x c^0(\text{tot})] = 0 \end{aligned} \quad (19)$$

Eqn. (19) yields an estimate of c.m.c._x ; c.m.c._y is obtained using eqn. (20) which follows from eqn. (16) using the assumptions noted above. Then

$$\begin{aligned} \text{c.m.c.}_y &= [\text{c.m.c.}_y^0 f(\text{mic}) / y(\text{aq})] \\ &\times \{1 - [\text{c.m.c.}_x y(\text{aq}) / \text{c.m.c.}_x^0 f(\text{mic})]\} \end{aligned} \quad (20)$$

Eqn. (19) and (20) are used to calculate c.m.c._x and c.m.c._y for the injected aliquot and for the contents of the sample cell at each injection. With reference to the latter, both c.m.c._x and c.m.c._y depend on the total concentrations of surfactant in the sample cell. A TURBO-BASIC computer program for a PC was used to calculate c.m.c._x and c.m.c._y . These two variables were calculated at each injection number. According to eqn. (18), $y(\text{aq})$ is related to $c(\text{aq; tot})$ which in turn depends on c.m.c._x and c.m.c._y .

Therefore the quadratic eqn. (19) was built within an iterative loop which started with the assumption that $y(\text{aq})$ is unity. Experience showed that five iterations were sufficient for each surfactant solution to obtain the required estimates of c.m.c._x and c.m.c._y . Then the overall c.m.c. for the mixture, $\text{c.m.c.}(\text{mix})$ is given by eqn. (21).

$$\text{c.m.c.}(\text{mix}) = \text{c.m.c.}_x + \text{c.m.c.}_y \quad (21)$$

For a given injection number, c.m.c._y , c.m.c._x and hence $\text{c.m.c.}(\text{mix})$ were calculated. The calculated $\text{c.m.c.}(\text{mix})$ was then compared with the total concentration of surfactant $c(\text{tot})$ in the sample cell. At low injection numbers the total concentration of surfactants X and Y, $c(\text{tot})$ in the aqueous solution held in the sample cell does not exceed the calculated c.m.c. whereas these concentrations exceed the c.m.c. for the solution in the injected aliquot. When the total concentration of surfactants X and Y in the sample cell $c(\text{tot})$ exceeds $\text{c.m.c.}(\text{mix})$, the calculation describes the injection of aliquots into the sample cell where both sample cell and injected aliquot contain a micellar phase. The injected surfactants X and Y distribute between aqueous and micellar phases. Then using the adjustable variables, $f(\text{mic})$ and g_{xy} , the injection number at the sharp change in $[q/(n_x + n_y)]$ identifying the c.m.c. is matched to the recorded injection number at this point, Fig. 1.

In the present context we note an important difference between the treatments of titration microcalorimetric data on the one hand for enzyme-substrate interactions¹ and on the other hand treatments of micelle deaggregation as described here. In the case of titration calorimetric investigations of enzyme-substrate interaction²³ (see also guest-cyclodextrin host interactions¹) a small aliquot of solution containing substrate is injected into the sample cell perturbing the chemical equilibrium involving free and bound substrate. The microcalorimetric results are analysed in terms of the extent to which the chemical equilibrium is perturbed. In the case of the systems considered here, the key process is the deaggregation of aggregates in the aliquot when injected into the sample cell containing, at least initially, water. Further, when the concentration of surfactant in the sample cell exceeds the c.m.c. the impact of the injected aliquot on the recorded heat is dramatically reduced.

Analysis of calorimetric data (enthalpies)

In the next stage of the calculation the target quantity is the change in the enthalpy of solution in the sample cell at injection number $(I + 1)$, $\Delta H(I + 1) = [H(I + 1) - H(I) - H(\text{inj})]$. The partial molar enthalpies of surfactants X and Y in the micellar phase, $H_x(\text{mic})$ and $H_y(\text{mic})$ depend on the mole fraction composition, $x_x(\text{mic})$ and $x_y(\text{mic})$. In real systems these partial molar enthalpies differ from the molar enthalpies of pure micellar surfactants, $H_x^*(\text{mic})$ and $H_y^*(\text{mic})$. The dependences of $H_x(\text{mic})$ and $H_y(\text{mic})$ on x_x $[=1.0 - x_y]$ were

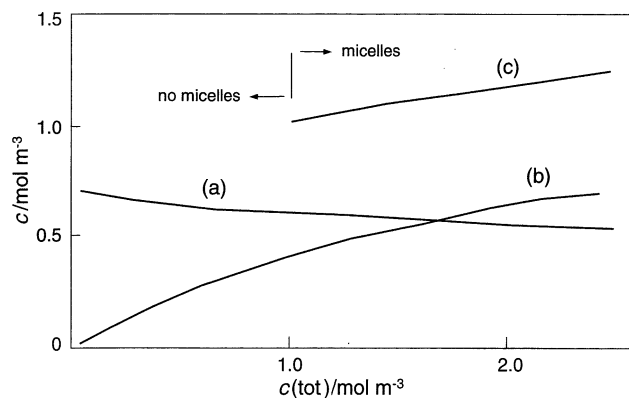


Fig. 3 Typical calculated dependence as a function of the total surfactant concentration in the sample cell, $c^0(\text{tot})$ for the mole fractions composition of the micellar phase; (a) CTAB and (b) TTAB. The plot refers to the enthalpogram recorded for 40 mol% CTAB where total amounts of surfactant in each aliquot were 4.6×10^{-8} (CTAB) and 6.9×10^{-8} (TTAB) mol.

expressed^{9,13} using eqn. (22) and (23) where U is an enthalpic interaction parameter. For ideal systems, U is zero.

$$H_X(\text{mic}) = H_X^*(\text{mic}) + [1 - x_X(\text{mic})]^2 U \quad (22)$$

$$H_Y(\text{mic}) = H_Y^*(\text{mic}) + [x_X(\text{mic})]^2 U \quad (23)$$

The partial molar enthalpies of surfactants X and Y, $H_X(\text{aq})$ and $H_Y(\text{aq})$ are related to the corresponding limiting partial molar enthalpies $\phi(H_X)^\infty$ and $\phi(H_Y)^\infty$ respectively and concentrations $c_X(\text{aq})$ and $c_Y(\text{aq})$. Several relationships were explored using pairwise enthalpic interaction parameters. In the event the simple forms shown in eqn. (24) and (25) proved adequate using a single interaction parameter.

$$H_X(\text{aq}) = \phi(H_X)^\infty + [h_{xy} c_X(\text{aq})] \quad (24)$$

$$H_Y(\text{aq}) = \phi(H_Y)^\infty + [h_{xy} c_Y(\text{aq})] \quad (25)$$

Adjustable parameters U and h_{xy} are used as variable inputs in the calculations.

Each aliquot of surfactant solution, volume $V(\text{inj})$ contains n_X^0 and n_Y^0 moles of surfactants X and Y respectively. Then the contribution of surfactants X and Y to $H(\text{inj})$ is given by eqn. (26).

$$\begin{aligned} H(\text{inj}) = & \text{c.m.c.}_X(\text{inj})V(\text{inj})H_X(\text{aq}) \\ & + [n_X^0 - \text{c.m.c.}_X(\text{inj})V(\text{inj})]H_X(\text{mic}; \text{inj}) \\ & + \text{c.m.c.}_Y(\text{inj})V(\text{inj})H_Y(\text{aq}) \\ & + [n_Y^0 - \text{c.m.c.}_Y(\text{inj})V(\text{inj})]H_Y(\text{mic}; \text{inj}) \end{aligned} \quad (26)$$

At low injection numbers I and $(I + 1)$, no micellar phase is present in the sample cell. Hence the contribution of the surfactants to the enthalpies of solutions in the sample cell are given by eqn. (27) and (28). Hence,

$$H(I; \text{low}) = n_X^0 H_X(\text{aq}) + n_Y^0 H_Y(\text{aq}) \quad (27)$$

And,

$$H(I + 1; \text{low}) = (I + 1)n_X^0 H_X(\text{aq}) + (I + 1)n_Y^0 H_Y(\text{aq}) \quad (28)$$

Combination of eqn. (26)–(28) yields

$$\begin{aligned} \Delta H(I + 1) = & -[n_X^0 - \text{c.m.c.}_X(\text{inj})V(\text{inj})]\Delta_{\text{mic}} H_X(\text{inj}) \\ & -[n_Y^0 - \text{c.m.c.}_Y(\text{inj})V(\text{inj})]\Delta_{\text{mic}} H_Y(\text{inj}) \end{aligned} \quad (29)$$

The microcalorimeter operates at constant pressure so the recorded heat $q(I + 1)$ equals $\Delta H(I + 1)$. The required quantity is the ratio, $\{q(I + 1)/[n_X^0 + n_Y^0]\}$. The structure of eqn. (29) is clarified if four assumptions are made with reference to surfactants X and Y: (i) $n_X^0 \gg \text{c.m.c.}_X(\text{inj})$, (ii) $\Delta_{\text{mic}} H_X(\text{inj}) = \Delta_{\text{mic}} H_X^0$,

(iii) $n_Y^0 \gg \text{c.m.c.}_Y(\text{inj})$, and (iv) $\Delta_{\text{mic}} H_Y(\text{inj}) = \Delta_{\text{mic}} H_Y^0$. Then,

$$\begin{aligned} q(I + 1)/[n_X^0 + n_Y^0] = & -[n_X^0/(n_X^0 + n_Y^0)]\Delta_{\text{mic}} H_X^0 \\ & -[n_Y^0/(n_X^0 + n_Y^0)]\Delta_{\text{mic}} H_Y^0 \end{aligned} \quad (30)$$

If for both surfactants X and Y, the standard enthalpies of micelle formation are exothermic, then $q(I + 1)/[n_X^0 + n_Y^0]$ is positive.

At high injection numbers, a micellar phase is present in the sample cell. The mole fraction composition of the micellar phase is not constant because it depends on the concentrations c_X^0 and c_Y^0 of the two surfactants in the sample cell. The analysis follows a pattern similar to that described above. We assume that both surfactants X and Y are present in the micellar phase in the sample cell.

$$\begin{aligned} H(I; \text{high}) = & \text{c.m.c.}_X(I)V(\text{cell})H_X(\text{aq}) \\ & + [n_X^0 - \text{c.m.c.}_X(I)V(\text{cell})]H_X(\text{mic}; I) \\ & + \text{c.m.c.}_Y(I)V(\text{cell})H_Y(\text{aq}) \\ & + [n_Y^0 - \text{c.m.c.}_Y(I)V(\text{cell})]H_Y(\text{mic}; I) \end{aligned} \quad (31)$$

For injection $(I + 1)$, we take account of the fact that c.m.c._X and c.m.c._Y differ from their values at injection number I .

$$\begin{aligned} H(I + 1; \text{high}) = & \text{c.m.c.}_X(I + 1)V(\text{cell})H_X(\text{aq}) \\ & + [(I + 1)n_X^0 - \text{c.m.c.}_X(I + 1)V(\text{cell})] \\ & \times H_X(\text{mic}; I + 1)\text{c.m.c.}_Y(I + 1)V(\text{cell})H_Y(\text{aq}) \\ & + [(I + 1)n_Y^0 - \text{c.m.c.}_Y(I + 1)V(\text{cell})]H_Y(\text{mic}; I + 1) \end{aligned} \quad (32)$$

In the resulting equation for $\Delta H(I + 1; \text{high})$ account is taken of the differences in amounts of surfactants in micellar form at injection numbers I and $(I + 1)$. The underlying pattern is indicated by eqn. (33) in the limit that the thermodynamic properties of aqueous and micellar phases are ideal.

We use eqn. (32) and (33) to calculate the difference between $H(I + 1; \text{high})$ and $H(I; \text{high})$

$$\begin{aligned} \Delta H(I + 1; \text{high}) = & -\text{c.m.c.}_X^0 V(\text{inj})\Delta_{\text{mic}} H_X^0 - \text{c.m.c.}_Y^0 V(\text{inj})\Delta_{\text{mic}} H_Y^0 \end{aligned} \quad (33)$$

Hence, using eqn. (30) and (33) we obtain the key difference in recorded heats.

$$\begin{aligned} [q(I + 1; \text{low}) - q(I + 1; \text{high})]/(n_X^0 n_Y^0) = & -[n_X^0/(n_X^0 + n_Y^0)]\Delta_{\text{mic}} H_X^0 - [n_Y^0/(n_X^0 + n_Y^0)]\Delta_{\text{mic}} H_Y^0 \end{aligned} \quad (34)$$

We note that the recorded ratio, $q(I + 1; \text{high})/(n_X^0 + n_Y^0)$ is not zero.

Results of calculations

The equations described above reproduce the essential features of the recorded enthalpograms using the parameters recorded in Table 1. The coefficient g_{xy} defined in eqn. (18) was for all CTAB + TTAB mixtures equal to 50 kJ mol⁻¹. The parameter $f(\text{mix})$ [$= f_X(\text{mic}) = f_Y(\text{mic})$; eqn. (17)] turned out to be an important variable in terms of determining the c.m.c. of the mixtures. For CTAB + TTAB mixtures $f(\text{mic}) = 0.7$ with the exception of the mixture containing 10% CTAB where $f(\text{mic}) = 0.8$. The remaining parameters depend on the composition of the surfactant mixtures; Table 1. Recorded and calculated enthalpograms are compared for three systems in Fig. 1. A slight disappointment is the way in which the calculated enthalpograms show a dramatic change in $[q/(n_X^0 + n_Y^0)]$ at the c.m.c. whereas the recorded plots show a smoother change. In fact, as commented above, the plots in Fig. 1 highlight the change in pattern of $[q/(n_X^0 + n_Y^0)]$ from low to high injection numbers whereas the corresponding van Os plots show that the change can be represented as more gradual. Nevertheless, the contrast in Fig. 1 of observed and

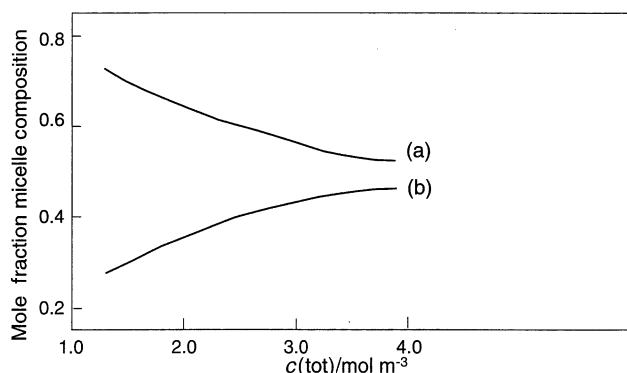


Fig. 4 Typical calculated dependence as a function of the total surfactant concentration in the sample cell, $c^0(\text{tot})$ for (a) c.m.c. of CTAB (b) c.m.c. of TTAB and (c) the total surfactant c.m.c.(mix). The point where $c^0(\text{tot})$ exceeds c.m.c.(mix) is indicated. The plot refers to an enthalpogram recorded for mixed surfactant containing 60 mol% CTAB where amount of CTAB = 4.2×10^{-8} mol and amount of TTAB = 2.8×10^{-8} mol in each aliquot.

calculated enthalpograms is, in part, a consequence of the model used in the calculations, which assumes that the system in the sample cell contains either a micellar phase (plus simple surfactant solutes in aqueous solution) or simple solutes. Interesting features underlying the calculated enthalpograms are highlighted in two examples shown in Fig. 3 and 4. Fig. 3 records the calculated c.m.c.s as a function of total concentrations of surfactants X and Y in the sample cell. Thus Fig. 3 shows the progress of the computer-based calculations based on eqn. (19) with reference to modelling a particular microcalorimetric titration. In this case, the surfactant comprised 60 mol% CTAB. The plot shows the separately calculated c.m.c.s of CTAB and TTAB as a function of the total surfactant concentrations in the sample cell, $c^0(\text{tot})$. Until $c^0(\text{tot})$ exceeds the calculated c.m.c. of the mixture, c.m.c.(mix) [cf. eqn. (21)], no micellar phase is present in the sample cell. This is the point in the microcalorimetric titration identified by a van Os plot. The interaction between surfactants both in solution and in micellar phase results in the dependence of c.m.c.(mix) on $c^0(\text{tot})$ for those systems where the micellar phase is present. Similar plots are obtained for all recorded enthalpograms. By contrast each van Os plot (e.g. Fig. 2) yields a single c.m.c. for a given mixture which is in effect a 'mean' c.m.c. for the mixture.

Fig. 4 shows the dependence of mole fraction composition (cf. eqn. (7)) of the micellar phase as a function of $c^0(\text{tot})$ where the surfactant contains 40 mol.% CTAB. Here the interaction parameters in micellar and aqueous phases describe the communication between the two surfactants producing a change

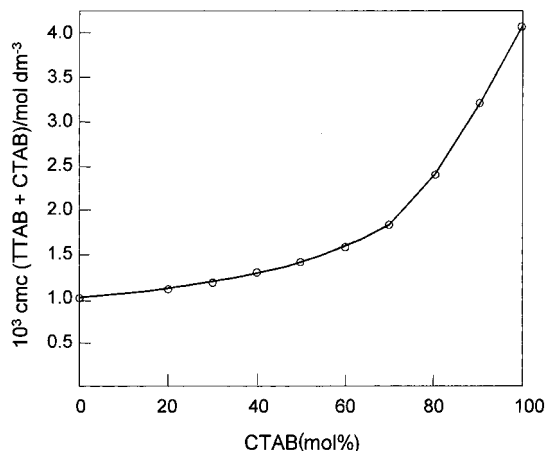


Fig. 5 Dependence on CTAB mol% of c.m.c.(mix) calculated using van Os plots for CTAB-TTAB mixtures at 298.2 K.

in mole fraction composition of the micellar phase as $c^0(\text{tot})$ increases. Thus, as more surfactant is added to the solution in the sample cell, the distribution of surfactants between aqueous and micellar phases results in a gradual change in the composition of the micellar phase. Across the mol% range, the calculated c.m.c. changes gradually with increase in mol% CTAB, Fig. 5.

Discussion

If surfactants X and Y existed in separate micellar phases within a mixed surfactant system, one might reasonably have expected enthalpograms which show breaks in pattern when the concentrations of surfactants in the sample cell exceed, in turn, c.m.c._x^0 and c.m.c._y^0 . This pattern is not observed. Hence we conclude that the micellar phase is a mixture containing both surfactants. Nevertheless, description of the thermodynamic properties of a mixed micellar phase presents problems bearing in mind that, in the present case at least, the two surfactants are salts. Therefore application of eqn. (22) and (23) to mixtures of ionic surfactants does raise questions. Indeed one might imagine that in a $\text{RN}^+\text{Me}_3\text{Br}^- - \text{R}'\text{N}^+\text{Me}_3\text{Br}^-$ mixture of micelles (where R and R' > C_8H_{17}) the micelle resembles a molten salt. Nevertheless Lopez-Fontan and co-workers²⁴ show that it is possible to treat the micellar phase formed by mixed ionic surfactants in terms used to describe a binary liquid mixture. Similar reservations must also be expressed in the context of the derivations of eqn. (14) and (15) which proceed on the basis that both surfactants X and Y are neutral rather than ionic surfactants. These reservations do not detract from the observation that the recorded enthalpograms can be accounted for on the basis of the properties of the separate surfactants together with a small set of parameters which describe surfactant-surfactant interactions in both micellar and aqueous phases. A key difference between calculated and recorded enthalpograms covers the region where the composition of the sample cell is characterised by the c.m.c. The recorded enthalpograms show a smooth rather than an abrupt change. Clearly, in a real system, the formation of a micellar phase is not as abrupt as described by the model developed here. As a system develops a micellar phase there is an initial tendency for the monomeric surfactants to cluster to form small aggregates which in turn cluster to form the micellar phase along the lines described by Huang and Verrall.²⁵ The model used here does not take account of such pre-micellar phenomena.

The derived parameters show several interesting features. We attribute the fact that $f(\text{mic})$ is less than unity (although positive by definition) to strong charge-charge stabilisation within the mixed micellar phase, a mixed 'molten' salt. In the calculation, the magnitude of $f(\text{mic})$ turned out to be crucial in matching observed and calculated enthalpograms. The positive g_{xy} indicates that the properties of the aqueous phase are dominated by surfactant-surfactant repulsion, possibly a consequence of hydrophobic mismatch between the surfactant cations.

An important test of the analysis would be offered by enthalpograms for mixtures of non-ionic and ionic surfactants which, we note, have enormous commercial importance. Unfortunately new complexities emerge as we have recently reported for enthalpograms recorded for non-ionic surfactants.²⁶

Clearly, detailed interpretation of the complete set of thermodynamic properties of mixed surfactant systems requires the development of an extensive database along the lines described here.

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